Enhanced luminance in polymer composite light emitting devices

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We demonstrate that mixing insulating oxide nanoparticles into electroluminescent polymer materials results in increased current densities, radiances, and power efficiencies in polymer light emitting diode devices. For low driving voltages, an order of magnitude increase in current density and light output is achieved with minimal loss in device lifetime. At 5 V, we achieve radiances of 10 000 cd/m^2 with external quantum efficiencies ~1% for nanoparticle/MEH–PPV composite films. © *1997 American Institute of Physics.* [S0003-6951(97)01335-1]

Polymer/nanoparticle composites have been increasingly studied because of their enhanced optical and electronic properties. Incorporation of CdSe and C$_{60}$ nanoparticles into a photoconducting material, such as MEH–PPV, can result in improved photovoltaic efficiency.[1,2] In addition, CdSe polymer composites can be used to make blue light emitters.[3,4] More recently, TiO$_2$ nanoparticles blended with electroluminescent organics have been shown to undergo lasing action with greatly reduced threshold pump powers.[5,6] Although our understanding of the effects of nanoparticles on the performance of electrooptic polymer devices is far from complete, it has been generally thought that the enhanced properties are due to either the ability of a group of nanoparticles to act as charge carriers, as electrooptically active centers, or as optical microcavities. In this paper, we demonstrate that nanoparticles can enhance the performance of polymer light emitting diodes (PLED) based primarily on structural effects. We demonstrate that this effect can result in low driving voltage, high radiance, and high efficiency devices.

The electroluminescent polymer used in the studies reported here was poly(2-methoxy-5(2′-ethyl)hexoxy-phenylenevinylene) (MEH–PPV) with a band gap of 2.1 eV. Polymer/nanoparticle composite films were made either by first dispersing the nanoparticles in the same solvent that the MEH–PPV is dissolved in, namely *p*-xylene, and then adding this mixture to the MEH–PPV/ *p*-xylene solution or by adding the nanoparticles directly to the MEH–PPV/*p*-xylene solution. The former technique resulted in better dispersion of the nanoparticles in the final film. Concentrations used varied from 1:4 to 2:1 weight ratios of nanoparticles to MEH–PPV; approximately 10% to 40% nanoparticles by volume. Our best results were obtained near 1:1 weight ratios. Nanoparticles tested included TiO$_2$ (rutile), TiO$_2$ (anatase), SiO$_2$ and Al$_2$O$_3$ with the polydisperse particle sizes ranging from 30 to 80 nm. The MEH–PPV nanoparticle/ *p*-xylene mixtures were spun cast onto an ITO coated glass surface coated with a polyaniline anode. The *p*-xylene solvent was then evaporated off, and Ca electrodes were deposited by thermal evaporation as described previously.[7] The diodes showed some inhomogeneities associated with nanoparticle aggregation; however, these inhomogeneities did not impede the overall performance of the device. Control samples containing no nanoparticles were made during every run for comparison, and film thicknesses were kept at 110±10 nm.

In Fig. 1, we show the radiance–voltage and current–voltage curves for the 1:1 TiO$_2$ (anatase)/MEH–PPV, 1:1 TiO$_2$ (rutile)/MEH–PPV, 1:1 SiO$_2$/MEH–PPV and for MEH–PPV film with no nanoparticles. The MEH–PPV film performance was consistent with previous results from several different groups also conducting polymer anodes.[7,8] For MEH–PPV films around 110 nm thickness, we consistently achieve turn-on voltages of 1.8 V, external quantum efficiencies on the order of 1%, current densities of 0.1 A/cm^2 and luminances above 1000 cd/m^2 at 5 V. We observe the same turn-on voltage for the composite light-emitting diodes; however, the exponential rise is considerably steeper such that by
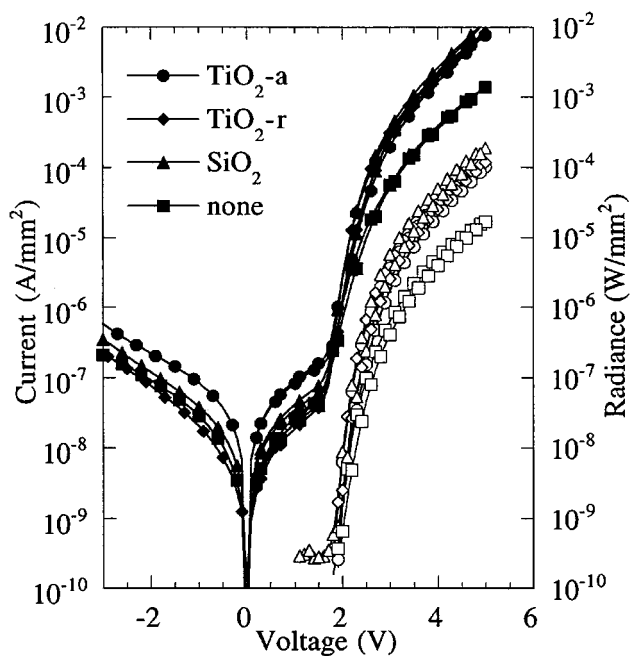

FIG. 1. Current–voltage and radiance–voltage curves for 1:1 TiO$_2$ (anatase)/MEH–PPV (circles), 1:1 TiO$_2$ (rutile)/MEH–PPV (diamonds), 1:1 SiO$_2$/MEH–PPV (triangles), and for MEH–PPV film with no nanoparticles (squares). Close symbols are for current. Open symbols are for radiance. 1 W/mm^2 = 7.3×10^7 cds/m^2.

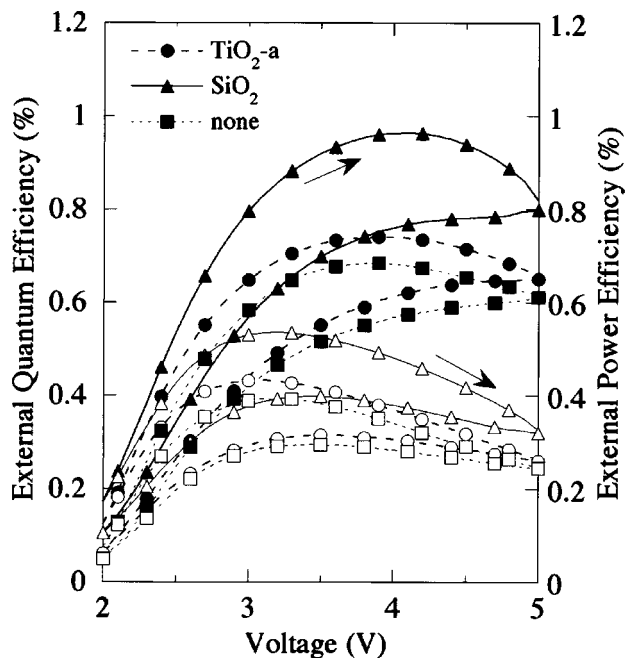[a]Electronic mail: sacarter@cats.ucsc.edu

FIG. 2. Quantum efficiency and power efficiency for 1:1 TiO$_2$ (anatase)/MEH–PPV (circles), 1:1 SiO$_2$/MEH–PPV (triangles), and for MEH–PPV film with no nanoparticles (squares). Close symbols are for external quantum efficiency. Open symbols are for external power efficiency.

4 V the diodes have luminance exceeding 1000 cds/m^2. By 5 V, we observed luminances exceeding 10 000 cd/m^2 at current densities of 1 A/cm^2, above which the diodes start to rapidly decay.

In Fig. 2, the external quantum and power efficiencies are plotted. Remarkably, the nanoparticle-based PLEDs achieve an *order of magnitude* increase in the light output and luminance with the *same* or even slightly higher external quantum efficiencies and with higher peak power efficiencies. The nanoparticles do not decrease the quantum efficiency as one might expect from the inclusion of such impurities inside the polymer matrix. Moreover, the composite diodes have unusually repeatable and stable performance up
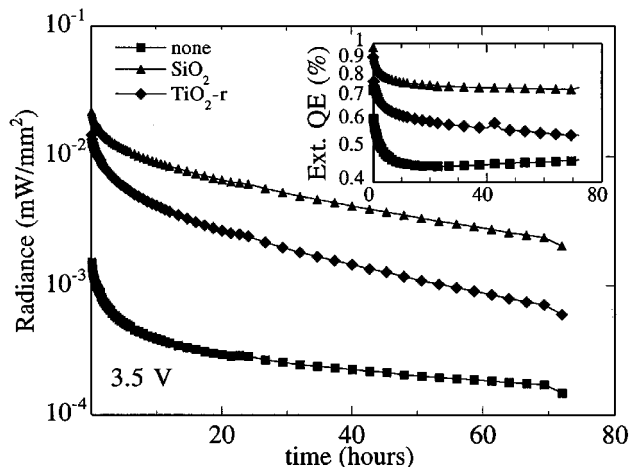

FIG. 3. Radiance aging curves at constant voltage 3.5 V for 1:1 TiO$_2$ (rutile)/MEH–PPV (diamonds), 1:1 SiO$_2$/MEH–PPV (triangles), and for MEH–PPV film with no nanoparticles (squares). Inset shows external quantum efficiency versus time.
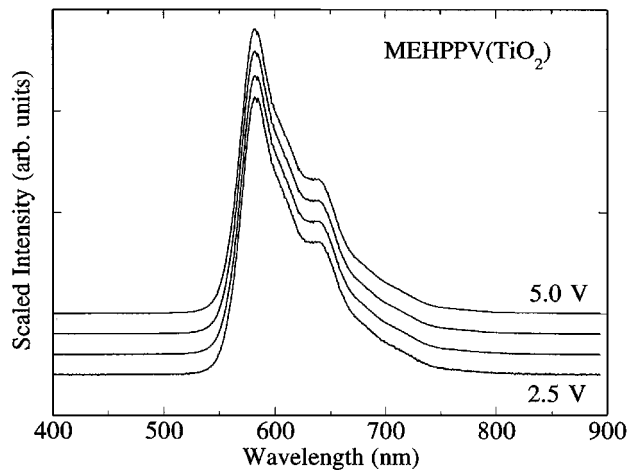

FIG. 4. Optical emission spectrum for 1:1 TiO$_2$/MEH–PPV as a function of driving voltage. Data sets are shifted and scaled for clarity. No change in the line shape of the optical spectrum is observed up to 5 V. (Detector saturates at driving voltages above 5 V.)

to continuous current densities of 1 A/cm^2. Slightly lower but similar performance can be achieved in very thin MEH–PPV films ($<$80 nm);[7] however, these diodes have short lifetimes and are not as repeatable since they tend to frequently develop shorts.

To examine the effect of the nanoparticles on PLED lifetime, the decay of the current and radiance as a function of time was measured with a constant driving voltage of 3.5 V. In Fig. 3, we plot the aging dependence of the radiance. In the short-term aging regime, we find that the nanoparticle diodes decay at a slower rate then the undoped MEH–PPV diodes even though the current densities are much higher. That indicates that the nanoparticles substantially change the nature of the short term decay. The long-term performance appears to be slightly worse for the nanoparticle films; this could be due to residual oxygen and water left on the surface of the metal oxide nanoparticle which causes photo-oxidation of the polymer and decay of the calcium electrode.[9,10] Also, the failure preferentially occurs where the nanoparticles are clumped in the films. We expect that better dispersion of the nanoparticles, better nanoparticle surface preparation, and switching to nonoxide nanoparticles will result in improved lifetimes that would exceed the undoped MEH–PPV diodes.

The question then is why do the nanoparticles so pronouncely improve the device performance? Given earlier results on TiO$_2$ particles in optically-pumped MEH–PPV films, it is possible that the improvement is coming from an enhancement by stimulated emission.[11] We tested this possibility by measuring the luminance spectrum with a grating spectrometer as a function of voltage where the diode was encased in a controlled dry nitrogen environment. In Fig. 4, the optical spectrum as a function of voltage from 2.5 to 5.0 V is shown. No evidence of line narrowing or changes in the line shape are observed at these voltages implying that the mechanism for improved performance is distinctly different from that found in optically-pumped TiO$_2$/MEH–PPV films.[6] As additional evidence, the particle densities used here are substantially higher than the densities of 10^{-2} used to achieve lasing action in MEH–PPV when

optically-pumped;[6] we find that nanoparticle densities of 10^{-2} cause no change in *electrically-pumped* MEH–PPV diodes. Also, little dependence was observed on the refractive index of the nanoparticle (1.6 for SiO_2 versus 2.0 to 3.0 for TiO_2 anatase and rutile, respectively). These observations lead us to conclude that optical scattering phenomenon is *not* causing the increase in performance. Also, such scattering cannot account for the observed increase in current density or the factor of 10 increase in light output. (Light loss by guiding for homogeneous films is of order $2n^2 \sim 6$ for SiO_2 and strongly dependent on n.) Another possible explanation is that the nanoparticle surfaces increase the probability of electron-hole recombination; however, again this would result in a change in the external quantum efficiency, rather than the current density as is observed.

A more consistent explanation for the improved performance is suggested by the change in device morphology caused by the incorporation of nanoparticles into the solution. During the spinning process, the nanoparticles can stick by strong electrostatic forces to the anode and to themselves, and capillary forces can then draw the MEH–PPV solution around the nanoparticles into cavities without opening up pinholes through the device. This will result in a rough surface over which the Ca electrode is evaporated and subsequently a large interface between the Ca cathode and the electroluminescent composite material. In the low voltage regime, charge-injection into MEH–PPV is expected to be cathode limited; the very steep rise in the I–V curves for the composite diodes suggests that more efficient injection at the cathode is occurring which could be caused by the rougher interface. For the higher-voltage regime, previous results have shown that transport in MEH–PPV appears to be bulk (or space-charge) limited and that thinner MEH–PPV films result in greater current densities and light output,[7] qualitatively similar to what we observe for the composite diodes. This data suggests that a likely explanation for the improved performance at higher voltages for our composite diodes is due to the effective thin spots which are created throughout the film by the capillary forces. Higher current densities, and subsequent higher light output, will flow through these areas.

Normally, these thin spots would result in rapid device failure, since they could enable the formation of shorts and hot spots through the film; however, the nanoparticle-based films are exceptionally stable with little evidence of shorts. This stability can be explained if the nanoparticles themselves can acts as physical barriers to current filaments or shorts forming in the sample. That is, they effectively cause the MEH–PPV to form a ''tortuous'' path through the composite film; this could explain the improvement in the short-term aging behavior if it is caused by either the formation and healing of shorts or by ionic diffusion (electrochemistry). This result leads to the conclusion that the best performing diodes will be obtained for dispersed nanoparticles at concentrations just below the percolation threshold in three dimensions. The percolation threshold should be around 25 % by volume for 2D systems and 50 % by volume for 3D systems for even thickness films. The lack of good dispersion and roughness in our films limits the estimate of the percolation threshold; nonetheless, the optimal results occurs for 1:1 ratio composites, close to the predicted percolation threshold in 3D given the relative densities of nanoparticles of 3 to 4 g/ml and MEH–PPV of 1.2 g/ml. We note this explanation of the results does not depend on the nature of the nanoparticles, as long as they remain electronically inactive. Similar results should be achieved by using nonoxide inorganic nanoparticles or polymer latex spheres of similar size and concentration, avoiding oxidation degradation induced by the nanoparticles themselves.

We have shown that the incorporation of nanoparticles inside an electroluminescent MEH–PPV thin film results in order of magnitude increases in current and luminance output. The nanoparticles appear to modify the device structures sufficiently to enable more efficient charge injection and transport as well as inhibiting the formation of current filaments and shorts through the polymer thin film. The composite nanoparticle/MEH–PPV films result in exceptionally bright and power efficient PLEDs; however, improvements are still needed in the device lifetime and homogeneity of the light output for these materials to be commercially viable.

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[11] The current densities are two to three magnitudes lower than what is expected to induce stimulated emission.

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